TECHNICAL REPORT NO. LWL-CR-01C73A

REDUCING THE FLAMMABILITY OF THE LWL SNOW STABILIZATION AGENT

Final Report

Contract No. DAAD05-73-C-0140

By
E. R. Evans
F. J. Sweeney

Franklin Institute Research Laboratories
Benjamin Franklin Parkway
Philadelphia, Pennsylvania 19103

April 1974

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U. S. ARMY LAND WARFARE LABORATORY
Aberdeen Proving Ground, Maryland 21005

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PREFACE

This report is submitted in compliance with contractual requirements as directed by the U.S. Army Land Warfare Laboratory, Aberdeen Proving Ground, Maryland, under Contract No. DAAD05-73-C-0140. Mr. Hugh T. Reilly, Applied Chemistry Branch, served as Technical Supervisor for the work, and we would like to acknowledge his insights and assistance during the project.

Principal Investigators for the program at The Franklin Institute Research Laboratories were Mr. F. J. Sweeney, Research Chemist, Materials and Physical Sciences Department and Mr. E. R. Evans, Multidisciplinary Projects Laboratory.

ABSTRACT

This report describes the results of a feasibility study to investigate reducing the flammability of methanol (methyl alcohol). Methanol has been used as a snow stabilization agent for helicopter landings and since dissemination of this agent might be from on board the helicopter, the relatively low flash point (16°C) was considered a flight safety hazard.

Of the candidate laboratory formulations evaluated, two appear promising as a replacement for methanol. They are (1) 55% ethylene glycol, 45% water and (2) 80% ethylene glycol, 10% water, 10% methanol. Both formulas have flash points above 38°C.

CONTENTS

FIGURES

1. INTRODUCTION

A. Background

Air mobility essential for military operations in snow covered environments is seriously hampered by blowing snow occurring when helicopters take off and land. The transition period which occurs when helicopters leave snow covered terrain to become airborne, and vice-versa for landing, is highly critical. Safety dictates that the pilot's vision and depth perception must be unimpaired. Mechanical aids and instruments have materially assisted in take off and landing operations, but greater assurance of visibility is needed. A clear view of the surface in front and below the aircraft is required. A means for rapid stabilization of snow that will, in a minimum of time, provide and maintain (for moderate time periods) adequate localized near-surface visibility for the operation of aircraft is required by Department of the Army personnel.

Under Contract No. DAAD05-73-C-0170, The Franklin Institute Research Laboratories (FIRL) investigated the feasibility of surface stabilization of snow.[1] The results of this program indicated that light, fresh snow can be stabilized by the application of a chemical agent. Snow surfaces treated with methanol (methyl alcohol) in concentrations as low as 1/2 ounce per square foot did not blow away when subjected to helicopter downdrafts of up to 72 miles per hour. In addition, the load bearing strength of the untreated snow (10 lbs/ft^2) was increased to approximately 135 lb/ft^2 after treatment.

Of the agents evaluated, methanol was found to be the most effective material in achieving snow stabilization as well as the most effective of the agents in increasing the load bearing strength of the snow.

At the conclusion of Contract No. DAAD05-73-C-0170, two successful field tests were conducted at Watertown, New York and Fort Wainwright,

Alaska. The aircraft (Huey) personnel reported that areas treated with methanol gave superior suppression to a possible "white-out" condition with ground visibility always present. The addition of a dye (violet color) to the methanol also gave the pilots a definitive form of reference when ground was heavily snow covered and no nearby markers were present.

B. Scope

Since the dissemination of the methanol will eventually be from on board the helicopter itself, the relatively low flash point* of the agent is considered a flight safety hazard.

The objective of this work effort was to modify the methanol by using additives or suppressives in order to increase its flash point from $16^{\circ}C$ to an acceptable $38^{\circ}C$ with $49^{\circ}C$ as the desirable limit.** In addition to a flammability evaluation, the modified agent parameters were to include:

1. Cost effectiveness
2. Viscosity
3. Rate of evaporation (volatility)
4. Dye stability
5. Storage characteristics
6. Corrosivity/Packaging

C. Methanol[2]

CH_3OH (methyl alcohol, carbinol) is the simplest of the saturated monohydric alcohols, with a molecular weight of 32.04. At room temperature it is water-white in color, neutral, mobile, flammable, volatile liquid with a characteristic odor.

Methanol is a highly polar compound, and is the closest alcohol in structure to water when considered as an organic derivative (R-OH).

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*The lowest temperature at which a combustible liquid will give off a flammable vapor that will burn momentarily.

** Flashpoint of Gasoline.

Boiling point, at 760 mm Hg, ^{o}C	64.51
Dielectric Constant at 20^{o}C	31.2
Explosive limits in air, vol. %	6.0 to 36.5
Flash point (ASTM Tag Open Cup), ^{o}C	15.6
Freezing point, ^{o}C	-97.49
Heat of combustion of liquid at 20^{o}C, kcal/mole	170.9
Ignition temp (apparent), in air, ^{o}C	470.0
Specific gravity at 20/4^{o}C	0.7915
Specific heat at 20^{o}C, cal/g	0.5996
Surface tension at 20^{o}C, dynes/cm	22.55
Vapor pressure at 25^{o}C, mm Hg	124.0
at 20^{o}C, mm Hg	97.0
Viscosity at 20^{o}C, cps	0.593

Figure 1-1. Physical Properties of Methanol

D. Theory of Snow Stabilization

Spraying methanol on snow surfaces initially causes melting of the snow crystals and particles. A slush is formed which then either refreezes into a hard ice surface or remains a heavy slushy fluid. In either case, the fine snow texture is appreciably modified and stability is accomplished. In the case of refreezing the reaction has been termed sintering[3] and the sintering mechanisms for ice are exceedingly complicated and poorly understood. The definitive evaluation of the concept was performed experimentally.

2. EXPERIMENTAL

A. Candidate Suppressants

The basic approach to increasing the flash point of methanol was to use a dilutant stocked within the U.S. Army's materiel stores, and in a quantity commensurate with a freezing point of not higher than $-40^{\circ}C$.

Figure 2-1 lists the vapor pressure and specific gravity of the four (4) candidate agents and methanol. Figure 2-2 contains the flash points of these agents.

VAPOR PRESSURES

Agent	mm of Hg	Temp. $^{\circ}C$
Methanol	97.0	20
Ethylene Glycol	0.06	20
Water	17.5	20
Freon TF[4]	205.0	20
Glycerol	0.00018	20

SPECIFIC GRAVITY

Agent	gm/cc	Temp. $^{\circ}C$
Methanol	0.792	20
Ethylene Glycol	1.115	20
Water	1.000	4
Freon TF	1.485	21
Glycerol	1.265	25

Figure 2-1. Vapor Pressure & Specific Gravity of Candidate Agents

Agent	Flash Point
Water	Boils at 100°C
Ethylene glycol	116°C, C.O.C.*
Freon TF solvent	Boils at 48°C
Glycerol	176°C*
(Methanol)	(18°C, T.O.C.**)

*Cleveland Open Cup, flash point procedure for materials having a flash point above 93°C.

**Tag Open Cup, flash point procedure for materials having a flash point below 93°C.

Figure 2-2. Flash Points of Candidate Agents

In Figures 2-3 through 2-7 which follow are presented the flash points of the candidate agents in solution.

The inability of water, ethylene glycol or glycerol to suppress methanol's flash point to a greater extent in higher percentages is attributed to the disparity in vapor pressures. In the attempt to use Freon TF solvent (Figure 2-7) as the suppressant, the flash points obtained were considered inconsistent and would require an extensive and separate investigation.

B. Other Considerations

Several other suppressive agents were considered during this work effort. The results of these evaluations are listed in Figure 2-8.

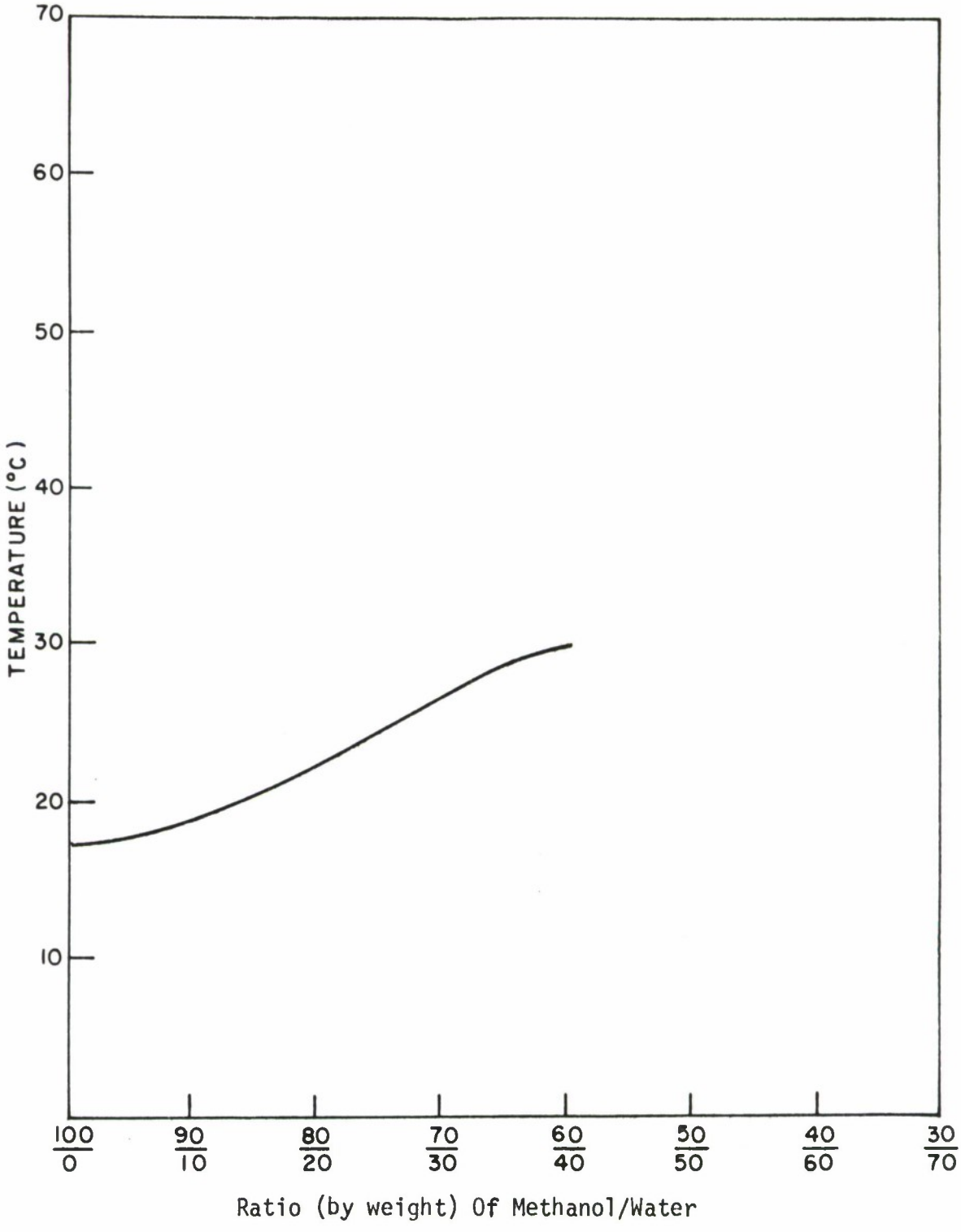

Figure 2-3. Flash Points of Methanol/Water Mixtures by Tag Open Cup

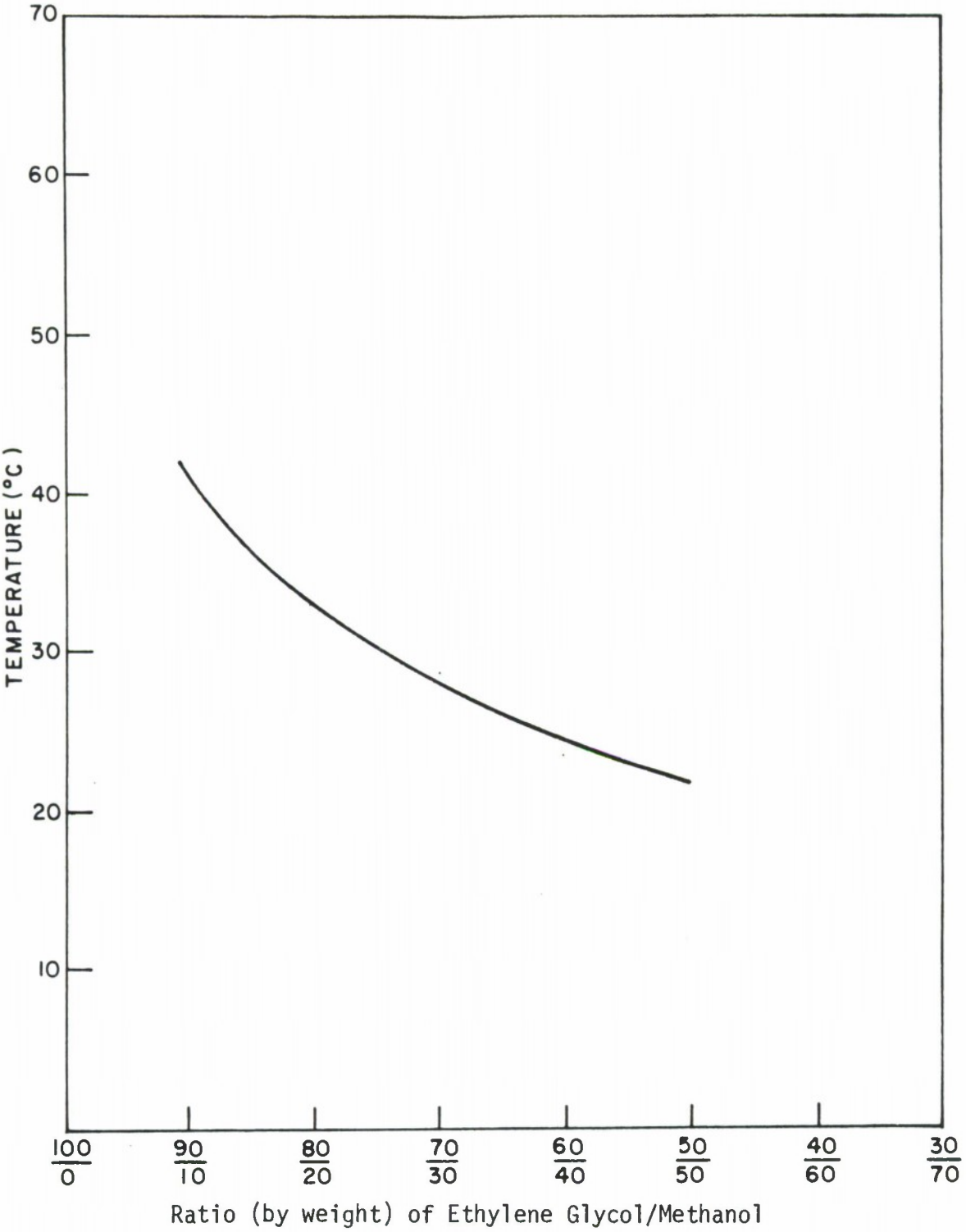

Figure 2-4. Flash Points of Ethylene Glycol/Methanol Mixtures by Tag Open Cup

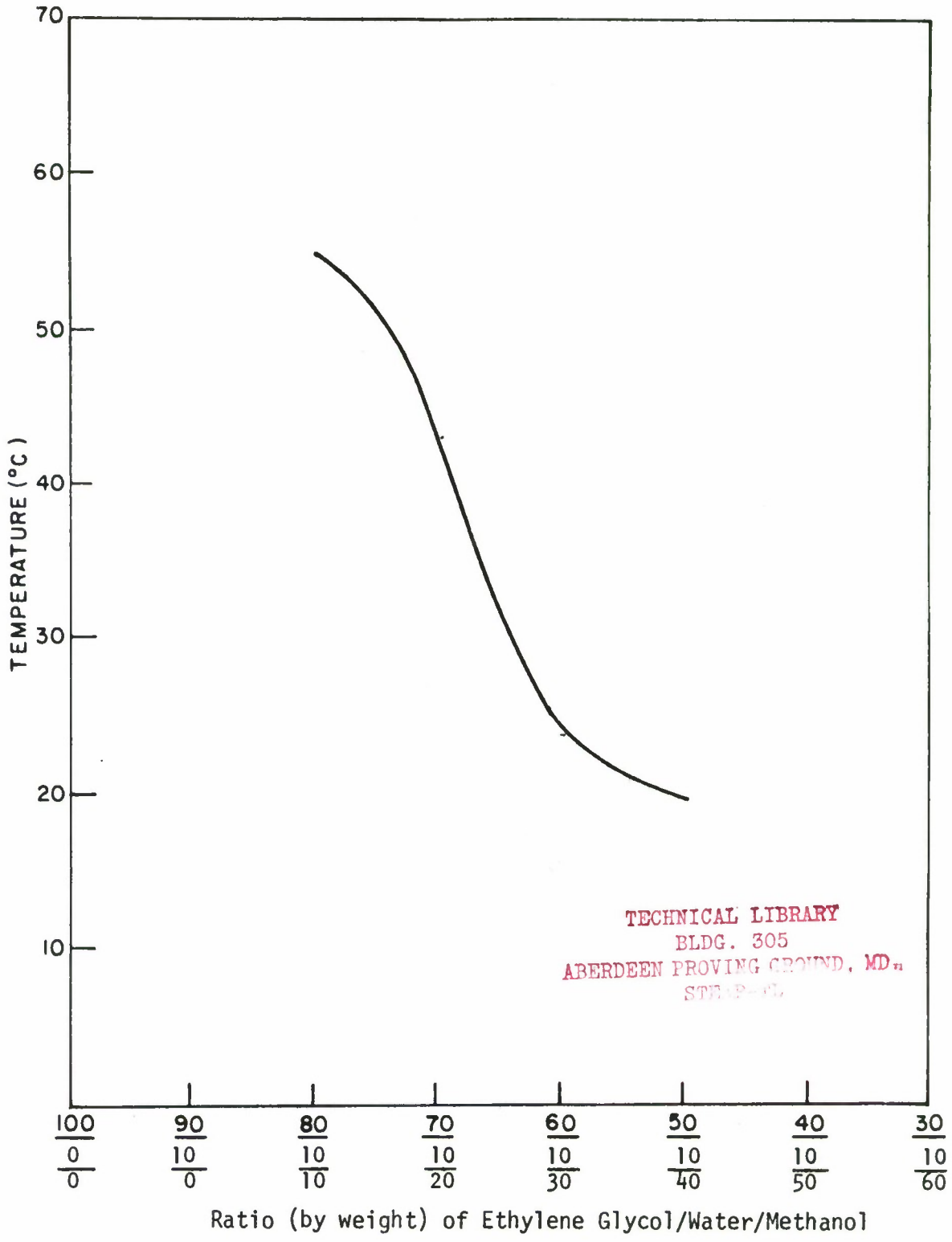

Figure 2-5. Flash Points of Ethylene Glycol/Water/Methanol Mixtures by Tag Open Cup

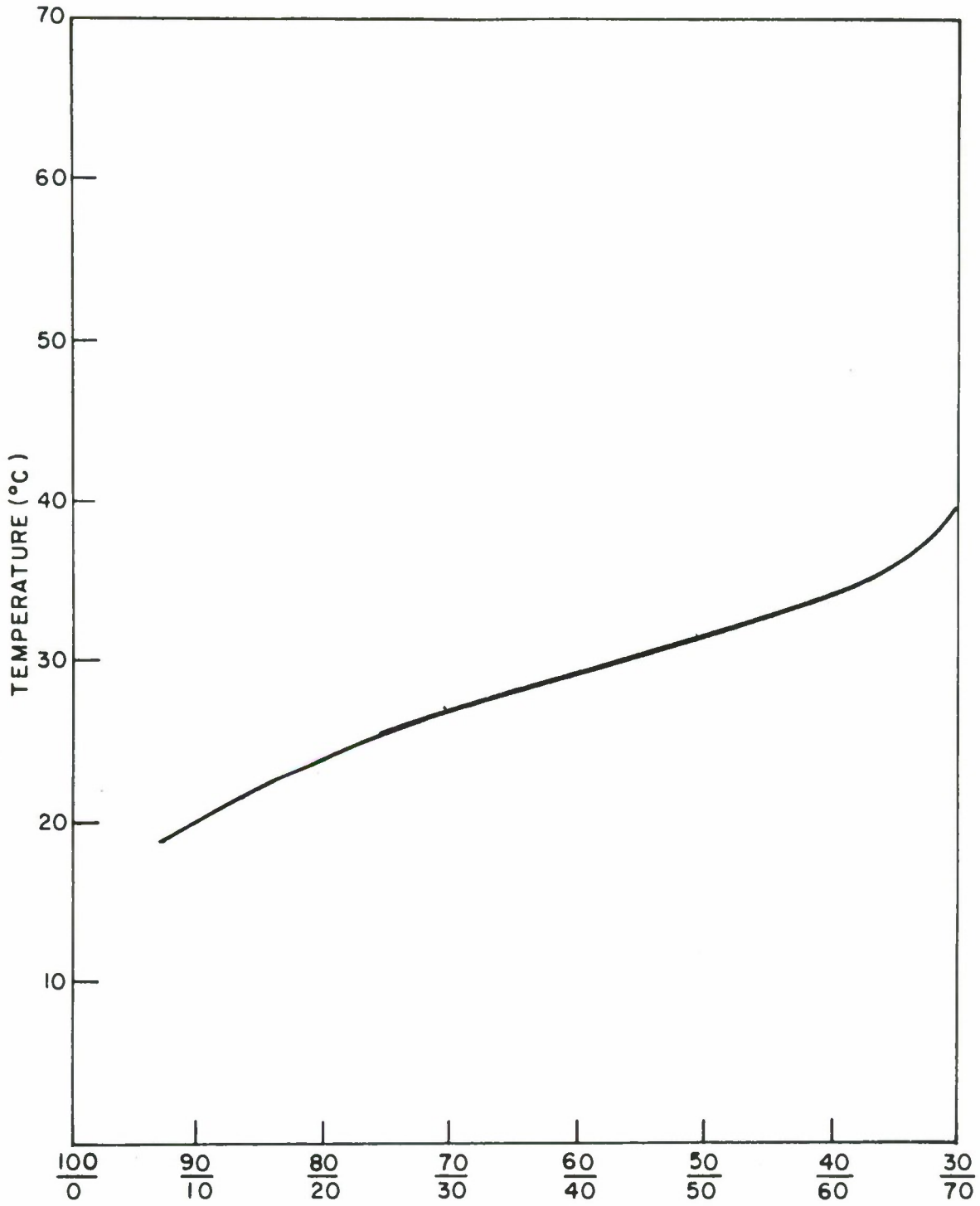

Figure 2-6. Flash Points of Methanol/Glycerol Mixtures by Tag Open Cup

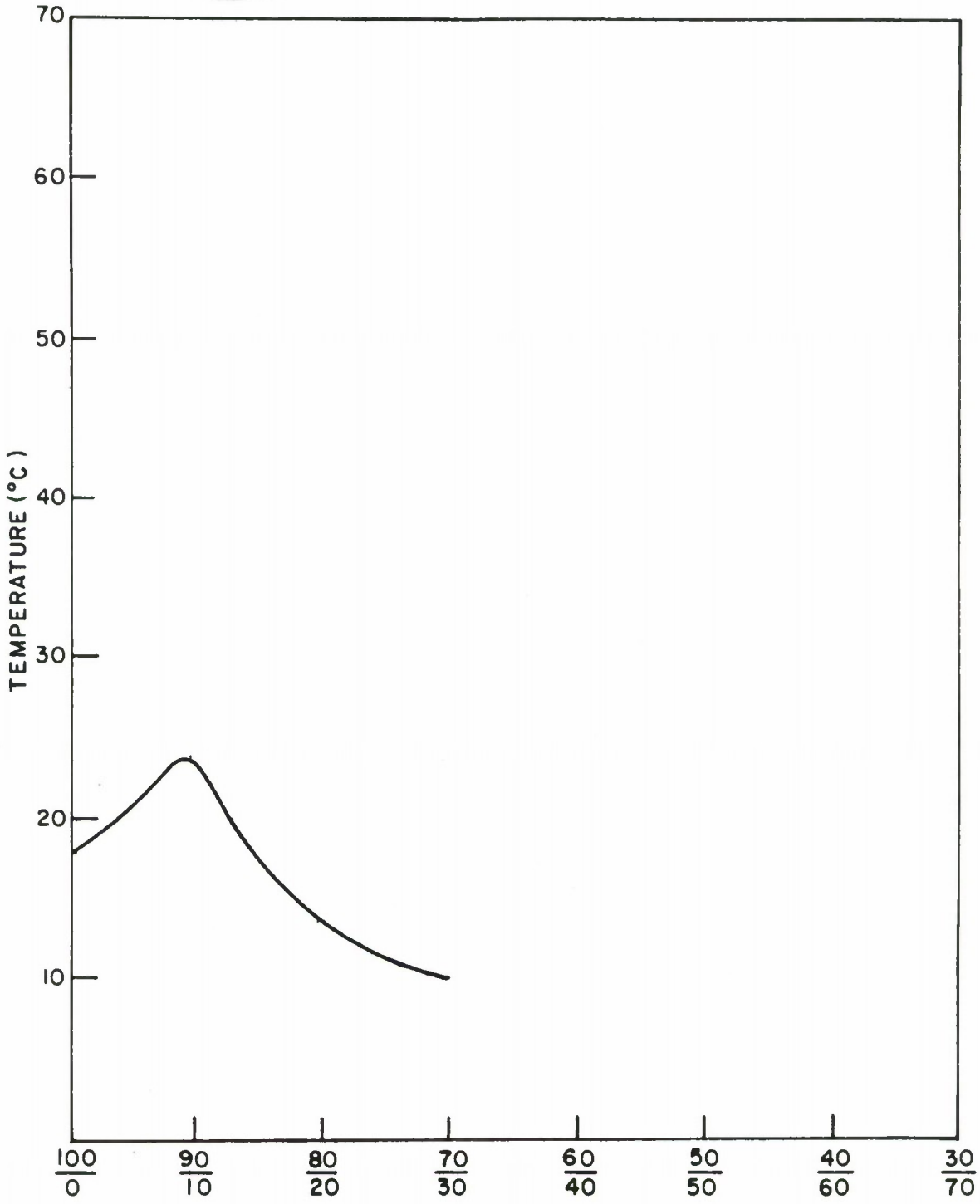

Figure 2-7. Flash Points of Methanol/Freon TF Mixtures by Tag Open Cup

	Agent	Remarks
1.	Carbon Tetrachloride	A 5% addition raised the flash point 7 °C, percentages above 5 would create a dangerous vapor problem.
2.	Inorganic Salts (Ammonia chloride, magnesium sulfate, etc.)	Their use within a dispensing system composed of more than one (1) metal would probably produce a corrosive effect.
3.	Higher Alcohols[5] (amyl, decyl, etc.)	These alcohols are essentially insoluble in water (snow).
4.	Urea	Has been used in dry form as a de-icer for runways; however, it will not melt ice at temperatures below 0 °C.
5.	Ethylene Glycol/Water	A mixture of 55% ethylene glycol, 45% (by weight) would give a maximum amount of water commensurate with a freezing point of -40 °C; see Figure 2-9 for ethylene glycol/water freezing point. The above formulation has a flash point above 60 °C and is self-extinguishing.

Figure 2-8. Evaluation of Other Considerations

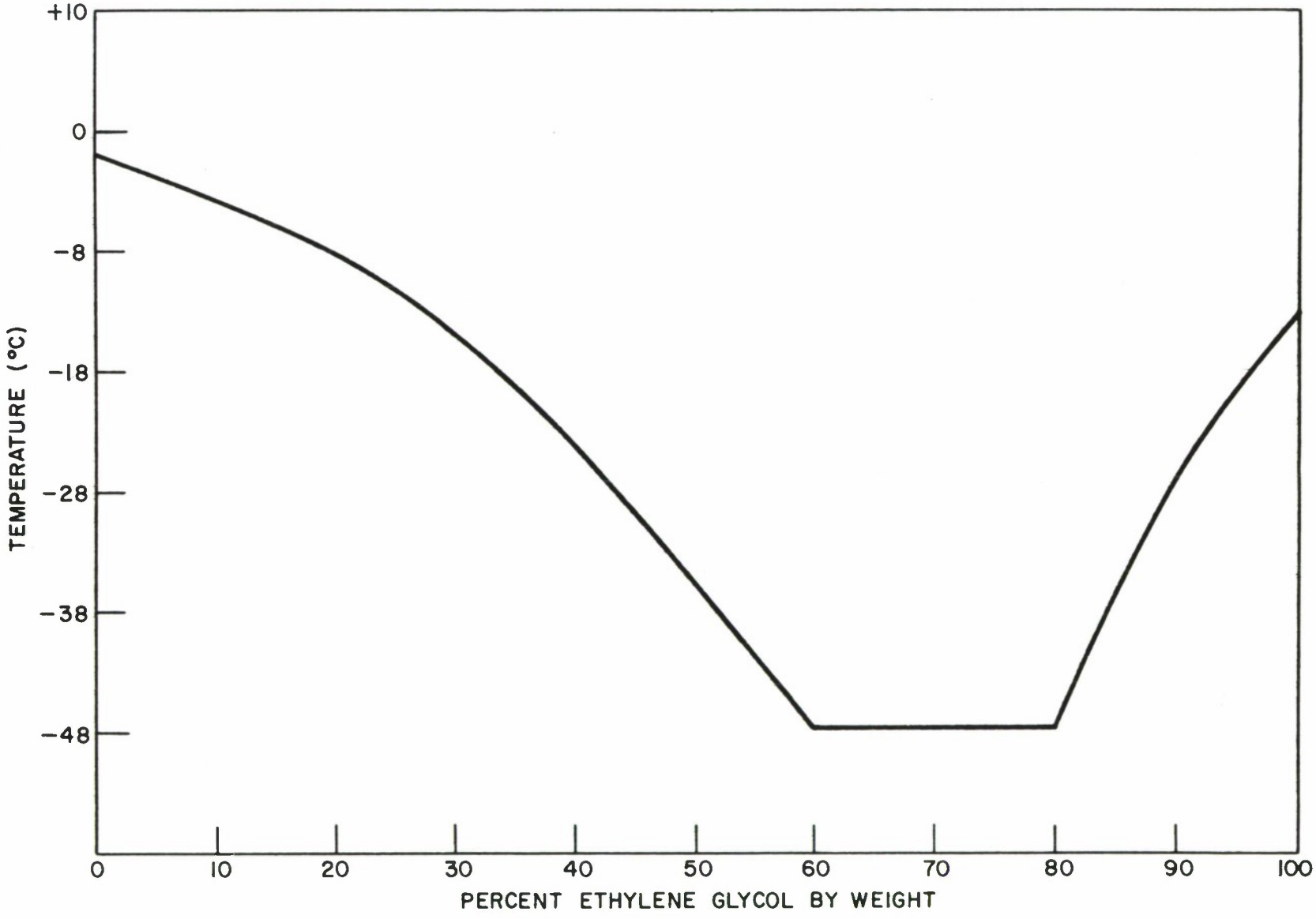

Figure 2-9. Freezing Points of Ethylene Glycol/Water Solutions[6]

C. Prospective Formulations

As a result of the flash point data obtained in Sections A and B, the following five formulations were considered acceptable for volability, viscosity and dye stability testing:

	Agent	% by Weight
1.	ethylene glycol	55
	water	45
2.	methanol	30
	glycerol	70
3.	ethylene glycol	90
	methanol	10
4.	ethylene glycol	80
	water	10
	methanol	10
5.	ethylene glycol	70
	water	10
	methanol	20

In Figure 2-10 that follows are presented the summation data for the prospective formulations and their comparison to methanol.

Formula % by Weight	(a) Viscosity (CP) (b) @ -30 to -35°C	@ 20°C	Specific Gravity gm/ml @ 20°C	Mole Fraction of H_2O	Flash Point °C	Volatility (time in min) % wgt lost at 20°C and 45% RH 15	30	45	60	Dye Stability (methyl red)	Remarks
Ethylene glycol 55 Water 45	81.6	10.5	0.97	0.73	60	3.93	6.97	9.12	13.05	good	Self-extinguishing flash point, consistency of 30W oil, candidate for field test.
Methanol 30 Glycerol 70	405.3	30.6	0.98	-	40	3.19	5.78	7.89	11.52	good	Very viscid; should not be considered for field test.
Ethylene Glycol 90 Methanol 10	Not obtainable	19.3	0.99	-	41	4.35	5.54	5.54	3.51	fair	Crystalliferous @ -20°C; absorbs atmospheric moisture, should not be considered for field tests.
Ethylene Glycol 80 Water 10 Methanol 10	96.0	14.8	0.98	0.26	54	4.80	7.42	8.76	9.65	good	Consistency of 30W oil; candidate for field test.
Ethylene Glycol 70 Water 10 Methanol 20	59.6(c)	16.5	0.99	0.24	42	11.45	16.73	18.47	19.27	good	Slightly crystalliferous @ -35°C possible candidate for field test.
Methanol	6	6	0.79	-	16	33.08	67.23	96.14	100	excellent	

(a) Brookfield Viscometer #1 spindle; (b) cold bath temp. variation, (c) probably due to crystals settling-out

Figure 2-10. Summation Data of Prospective Formulations

3. COST EFFECTIVENESS AND CORROSIVITY

The three commercial additives used in the flammability reduction program are readily available in bulk quantities. As of this report date, their price listings were as follows:

Item			
Ethylene glycol	1 dr. = $ 80.26,	3 or more drs.	$69.96
Glycerol	" = 166.73,	" " " "	161.03
Methanol	" = 35.10,	" " " "	31.80

All prices f.o.b. Philadelphia, Penna.

Since all three additives have been extensively used, both singly and in combination with water in various metallic and plastic systems, the possibility of corrosion within any spray system is considered remote.

4. CONCLUSIONS

As a result of this flammability reduction program conducted under Task Assignment No. 9 of Contract DAAD05-73-C-0140, the following conclusions may be made:

1. That the flash point of methanol could not be desirably raised to (49°C) by the addition of small quantities of the selected stock items and that additives above fifty per cent (50%) were required to reach a minimum flash point of 38°C.

2. That of the five prospective formulations obtained, two contain ten per cent (10%), one contains thirty per cent (30%), one twenty per cent (20%) and one zero per cent methanol.

3. The results obtained with Freon TF solvent were inconsistent.

4. That ethylene glycol/water (55/45) and ethylene glycol/water/methanol (80/10/10) formulations were the most fluid at -30°C having viscosities of 81.6 and 96.0 centipoises respectively.

5. RECOMMENDATIONS

1. That USALWL obtain the airborne spray equipment and test quantities of the following two formulations for cold chamber nozzle testing at the Aberdeen Proving Ground, Test and Evaluation Command facilities.

(a)	ethylene glycol	55
	water	45
(b)	ethylene glycol	80
	water	10
	methanol	10

2. That simultaneously with the above, a program be conducted using the same formulations and the original ground spray system to assess the snow stabilization characteristics of the proposed two new formulas.

6. REFERENCES

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3. Ramseier, R. O., Sander, G. W., *Sintering of Snow as a Function of Temperature*, Symposium of Davos 1965.

4. E. I. DuPont and Co., Bulletin No. FST-1, *Freon* TF Solvent Data.

5. Enjay Chemical Co., Bulletin on Oxo Alcohol, 1972.

6. Union Carbide Corp., Data Booklet on Prestone, 1972.

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